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**AN EVALUATION OF THE METHOD TO DETECT
URANIUM HEXAFLUORIDE IN THE
EFFLUENT GASES FROM THE PURGE CASCADE**

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**Materials and Chemistry Technology
Process Support Division**

April 16, 1982

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AN EVALUATION OF THE METHOD TO DETECT URANIUM
HEXAFLUORIDE IN THE EFFLUENT GASES FROM THE PURGE CASCADE

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INTRODUCTION

Various gases in the gaseous diffusion cascade produce a variety of gaseous compounds that appear at the top of the purge cascade. Difficulties have been experienced in interpreting the analytical results obtained from a Dupont 400 UV Photometric Analyzer which is used to monitor the concentration of UF_6 in the purge cascade effluent. The purpose of the present work was to obtain information that might reasonably explain the cause of uncertainties experienced in these gas analyses and, to some extent, to recommend possible solutions to the problem.

In the gaseous diffusion plant, gases having molecular weights considerably below that of UF_6 are transferred very effectively to the top of the cascade. The accumulation of light gases at the top of the cascade would seriously block the withdrawal of product from the plant. In order to avoid this problem, a section of the cascade just above the top withdrawal point is used as a top purge cascade, the purpose of which is to separate the light gases from the UF_6 and to dispose of them in some manner.

Disposition of the light gases must be done under controlled conditions so that loss of the UF_6 does not occur. In order to determine whether or not these conditions are adequate, a Dupont 400 Photometric Analyzer is used at ORGDP to detect whether UF_6 is present in the discharge stream of the purge cascade. After the Dupont analyzer had been in use for some time, it was noted by operations personnel that under certain operating conditions in the cascade, ambiguities were detected in the analyses. A discussion of the problem between Process Support and Operations personnel resulted in the hypothesis that some constituent other than UF_6 might at times be interfering with the UF_6 analysis, thus giving false readings for UF_6 concentration.

EXPERIMENTAL

Normally, a portion of the discharged gases is drawn into a small cell at some pressure and cell length suitable to detect UF_6 in the parts per million range. In order to facilitate making these measurements, the cell is fitted with sapphire windows, placed in the sample compartment of a Dupont 400 Photometric Analyzer, and then evacuated. A beam of ultraviolet radiation is allowed to pass through the cell to a semi-transparent mirror which splits the beam into two directions. The two beams are directed through optical filters, one of which (measuring filter) allows only radiation at the wavelength of interest to pass through to a photo detector. The second beam filter allows only radiation at the reference wavelength to pass through to a second photo detector. While the cell is evacuated, an electrical balance can be achieved where the output from each detector will be the same and an optical null can be

measured on a recorder. When UF_6 is admitted into the cell, the recorder deflection will be proportional to the UF_6 partial pressure. Since the reference filter is selected to pass radiation at a wavelength (361 nm) not affected by UF_6 absorption, no change in the intensity will occur to its detector and the output level will remain the same. The measuring filter, however, has been selected to transmit a wavelength (228 nm) which is characteristically absorbed by the UF_6 , thus reducing the intensity of the beam reaching the detector. This causes a voltage imbalance between the two detectors and results in the recorder deflecting to some new level. The amount of this deflection is a function of cell length and UF_6 gas pressure.

Gases known to be present in the plant stream were analyzed and complete UV spectra (800 nm to 200 nm) were made on the Beckman UV 5270 spectrophotometer located in Materials and Chemistry Technology. This instrument incorporates a dual beam, grating mode of operation covering the UV range, 800 to 190 nm. A continuous absorption spectrum was recorded for each gas at various pressures at a constant cell length of 60 mm to calibrate the instrument. The cell was equipped with sapphire windows. Figures 1-16 show the absorption spectra in the range 800-200 nm for the sixteen gases analyzed.

RESULTS AND DISCUSSION

The accompanying table lists the gases that were examined. The absorbance per torr pressure was calculated for each gas at the standard measuring and reference wavelength positions, 228 and 361 nm, respectively.

As shown in Table I, gases other than UF_6 do absorb in the UV at 228 and 361 nm. The varying concentrations of these gases in the plant stream would result in erroneous values thought to be due to UF_6 gas, especially if the concentration of UF_6 is at a very low level. For example, absorption at 228 nm due to the gases ClO_2F , ClF_3 , and ClF would bias absorption measurements too high or in other words, the actual amount of UF_6 would be less than indicated. Conversely, Cl_2 , ClF , and COF_2 absorption at 361 nm would result in a reference signal suppression, thus causing the absorption measurement to be biased too low.

Examination of the UV spectra obtained from the Beckman UV 5270 spectrometer revealed that at 500 nm, none of the gases tested absorbed in this region. It would thus be feasible to obtain a new reference filter with a value of 500 nm instead of the present filter at 361 nm, thus eliminating absorption by other gases at the reference wavelength and eliminating that bias in the UF_6 analysis.

Unfortunately, UF_6 absorbs strongly in the UV only in the 228 nm region. Thus, no substitute measuring filter may be used. A correction for absorption occurring at 228 nm by gases other than UF_6 would be necessary and may be done by (a) determining the partial pressure of each gas by infrared absorption and mass spectroscopy and then subtracting the sum of the partial pressures of these gases from the total sample pressure and assuming the difference is due to UF_6 , (b) by measuring the total absorbance at 228 nm and then subtracting the residual absorbance remaining after UF_6 is removed from the gas sample by cold trapping or by a chemical absorption method.

In summary, Table I shows ten gases found in the plant stream which could influence the UF_6 absorption measurement under certain conditions in the plant operation. An absorbance correction would be necessary for the filters at 228 nm and 361 nm wavelengths to offset the absorption of these gases from absorption due to UF_6 . In the event that a filter designed to operate at 500 nm were used instead of 361 nm, then correction for absorbances at 228 nm only would be necessary.

CONCLUSIONS

Certain gases have been found in the purge cascade that do absorb at the UV wavelength characteristic of UF_6 as well as at the wavelength that has been used as a reference. The two filters employed in the Dupont 400 Analyzer transmit radiation at wavelengths 228 nm and 361 nm respectively. None of the cascade gases absorb at certain regions in the UV spectrum, such as 500 nm, so that a filter allowing UV transmission at 500 nm would be suitable for the reference position.

An alternate method of determining the UF_6 in the purge effluent may be employed by measuring the UF_6 content directly by infrared absorption using a cell of suitable length. The fact that in the UF_6 infrared spectrum, absorption bands occur at several wavelengths which differ in wavelength from the other gases tested, thus giving several opportunities to measure the UF_6 absorbance.

Table I

ABSORBANCE PER UNIT PRESSURE FOR PURGE CASCADE GASES
AT STANDARD MEASURING AND REFERENCE WAVELENGTHS

<u>GAS</u>	<u>ABSORBANCE* AT 1 TORR PRESSURE</u>	
	<u>228 nm</u>	<u>361 nm</u>
1. F-115	0.0000	0.0000
2. COF ₂	0.0001	0.0001
3. ClO ₂ F	0.2441	0.0000
4. SiF ₄	0.0000	0.0000
5. CF ₄	0.0000	0.0000
6. F ₂	0.0012	0.0003
7. HF	0.0025	0.0002
8. ClF ₃	0.1040	0.0006
9. UF ₆	0.4500	0.0000
10. F-12	0.0000	0.0000
11. F-13	0.0000	0.0000
12. F-114	0.0001	0.0000
13. F-116	0.0000	0.0000
14. ClF	0.0265	0.0043
15. Cl ₂	0.0000	0.0098
16. HCl	0.0002	0.0000

*Absorbance defined as $A = \log_{10} \frac{1}{T}$, T is transmittance. $T = I/I_0$.

Where I and I₀ are intensities of transmitted and incident radiation.
Percent transmittance, %T = 100T. Infrared cell length 60 mm, equipped
with sapphire windows.

DWG. NO. K/G-82-1132
(U)

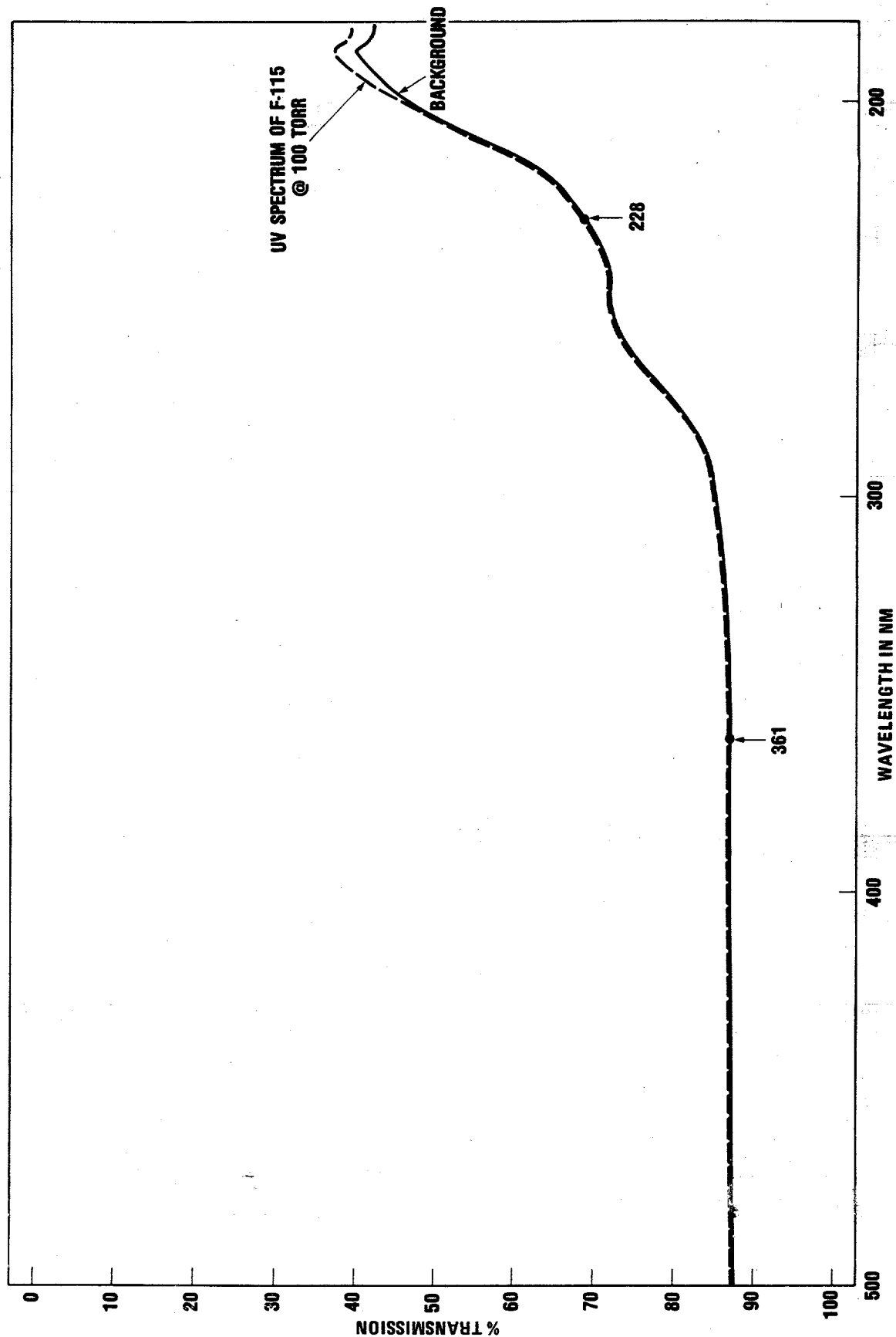


Figure 1
UV SPECTRUM OF F-115 @ 100 TORR

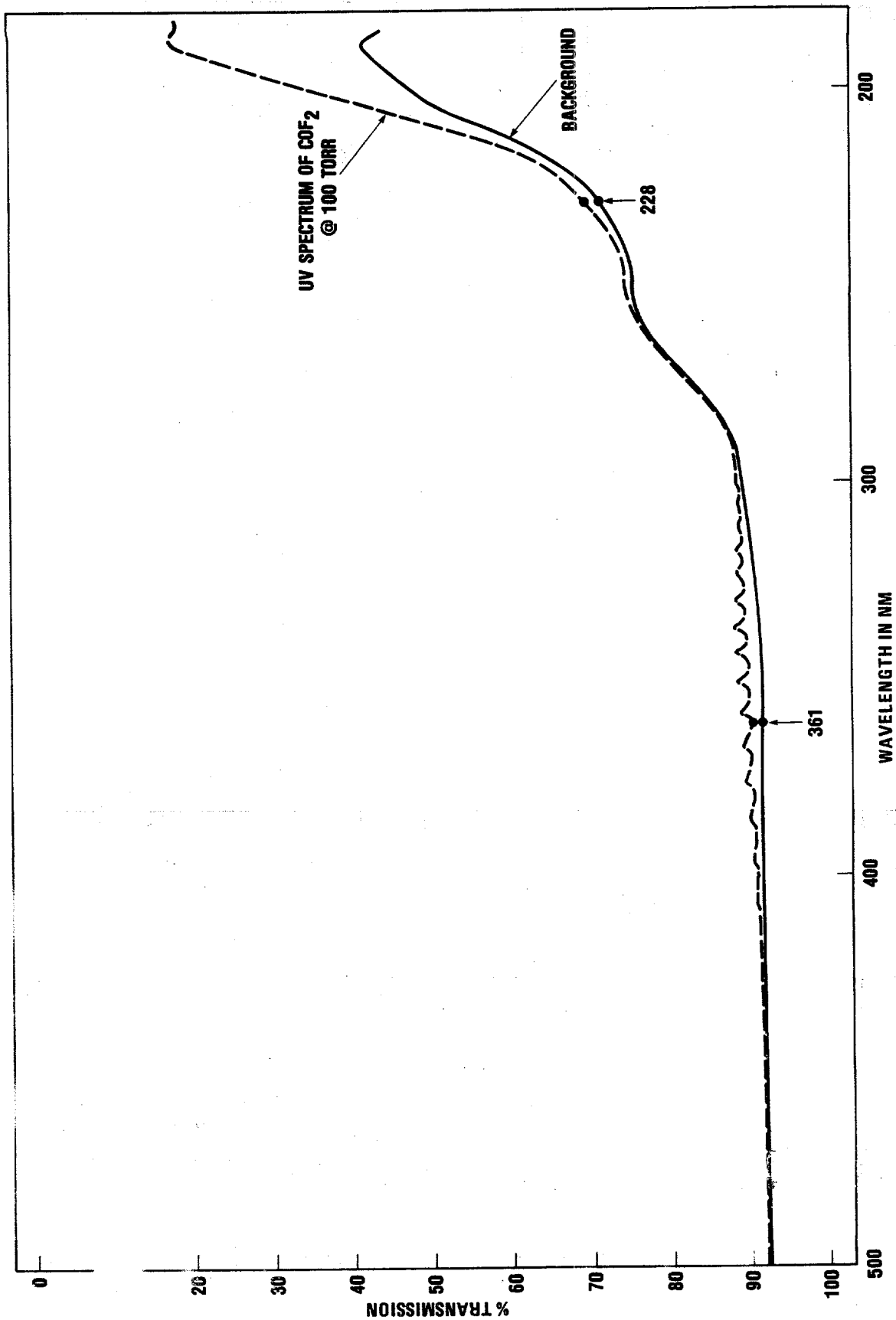
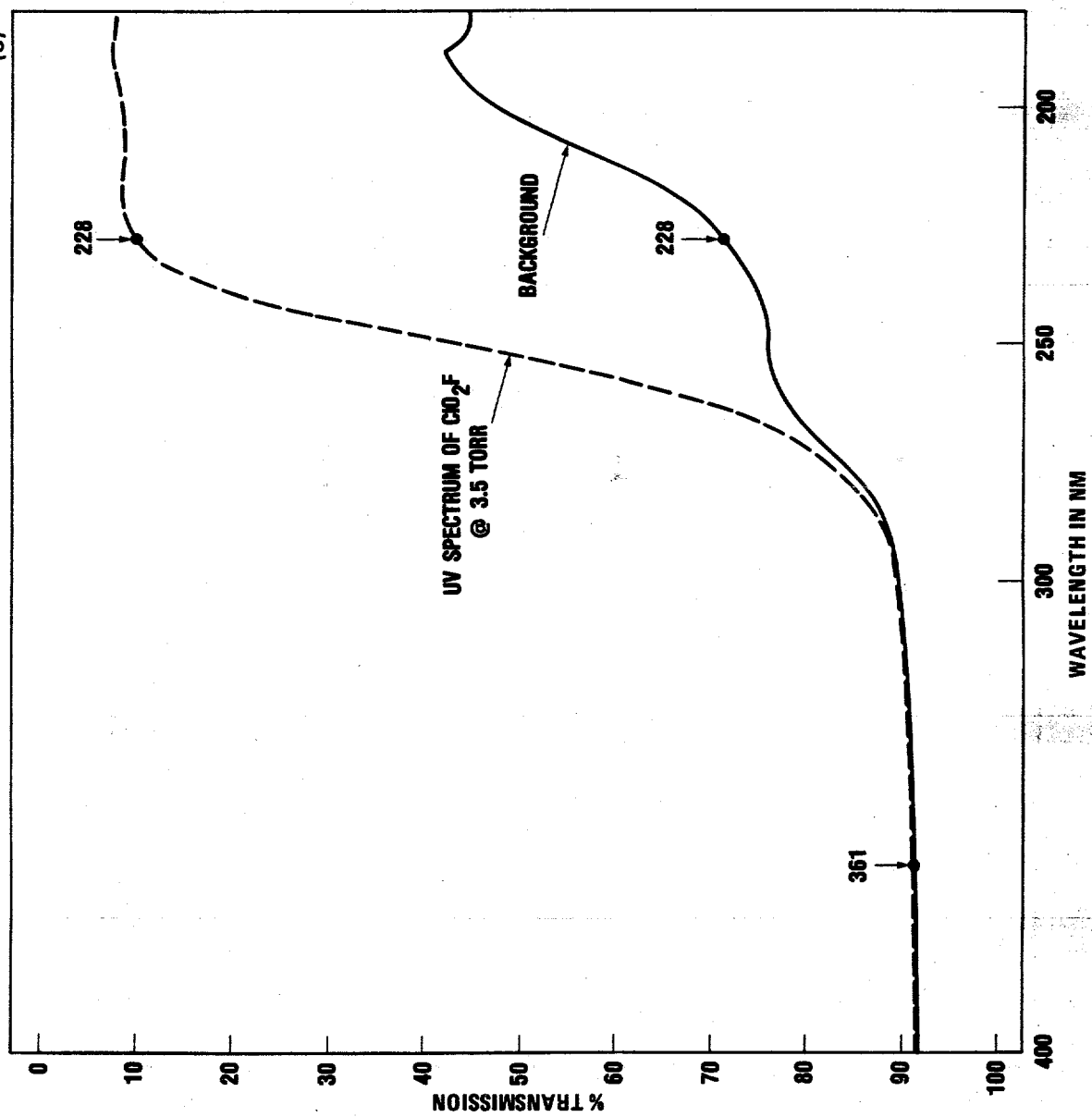
DWG. NO. K/G-82-1131
(U)

Figure 2
UV SPECTRUM OF COF_2 @ 100 TORR

DWG. NO. K/G-82-1135
(U)Figure 3
UV SPECTRUM OF ClO_2F @ 3.5 TORR

DWG. NO. K/G-82-1134
(U)

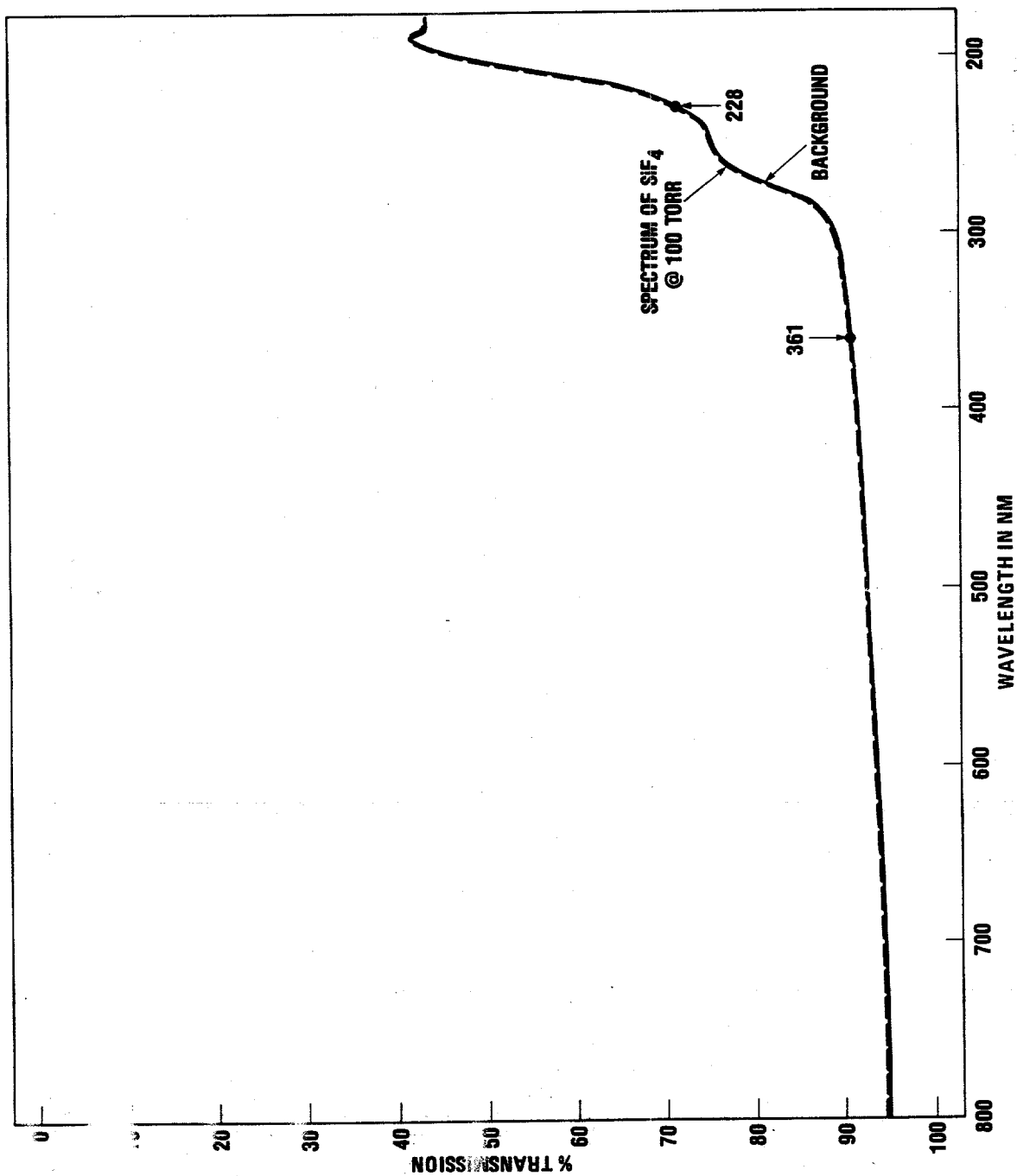


Figure 4
SPECTRUM OF SiF₄ @ 100 TORR

DWG. NO. K/G-82-1146
(U)

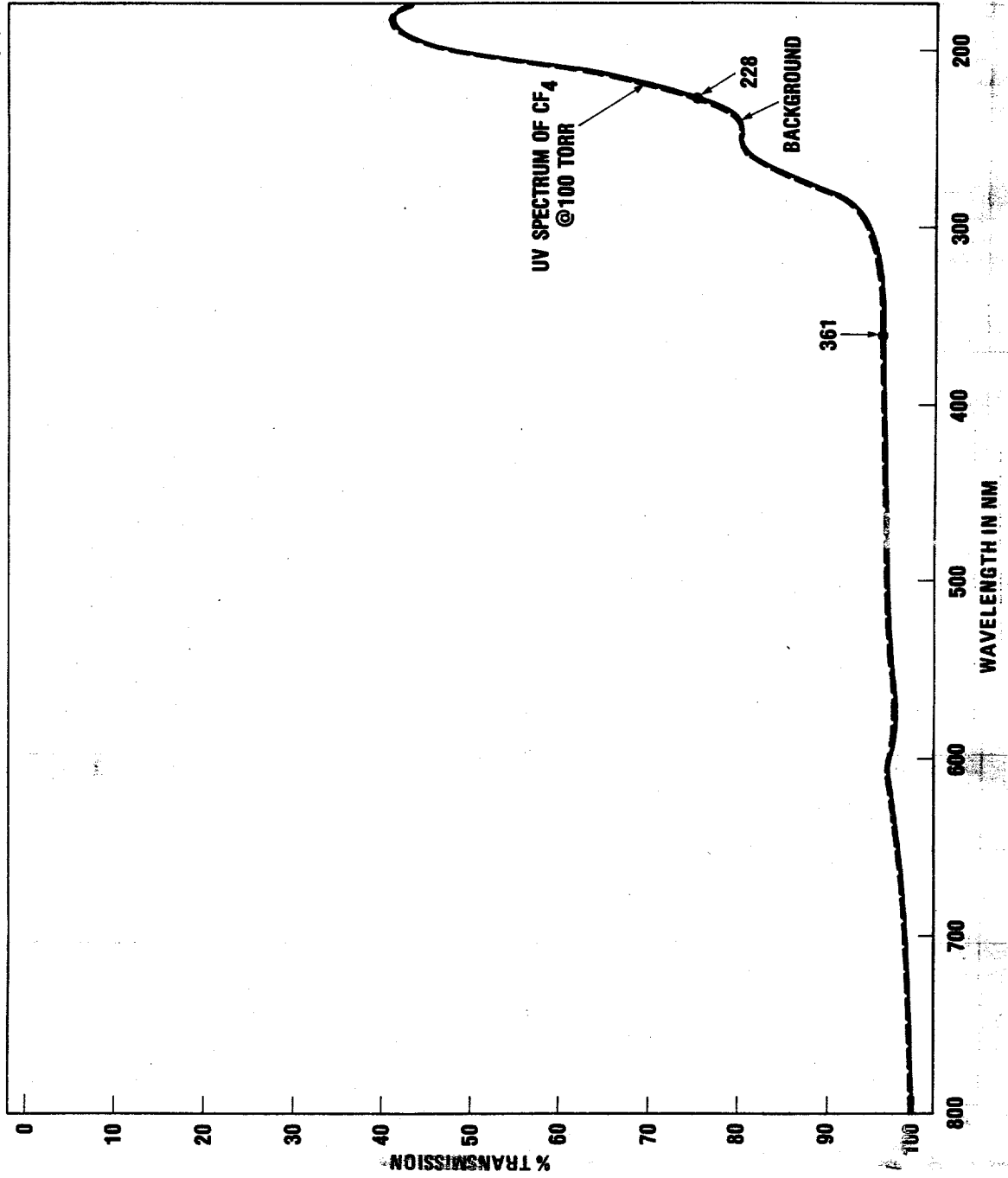


Figure 5
UV SPECTRUM OF CF_4 @ 100 TORR

DWG. NO. K/G-82-1145
(U)

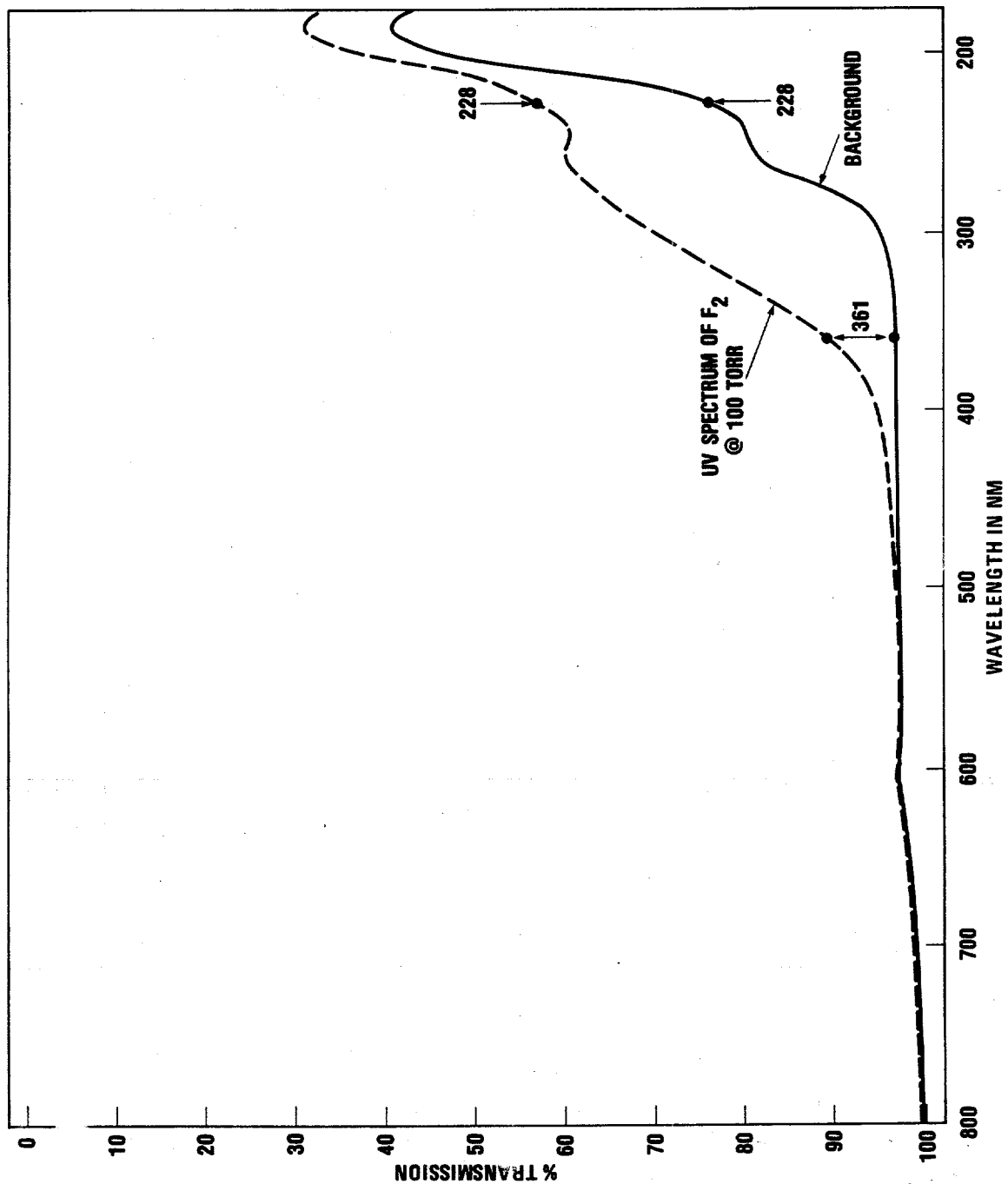
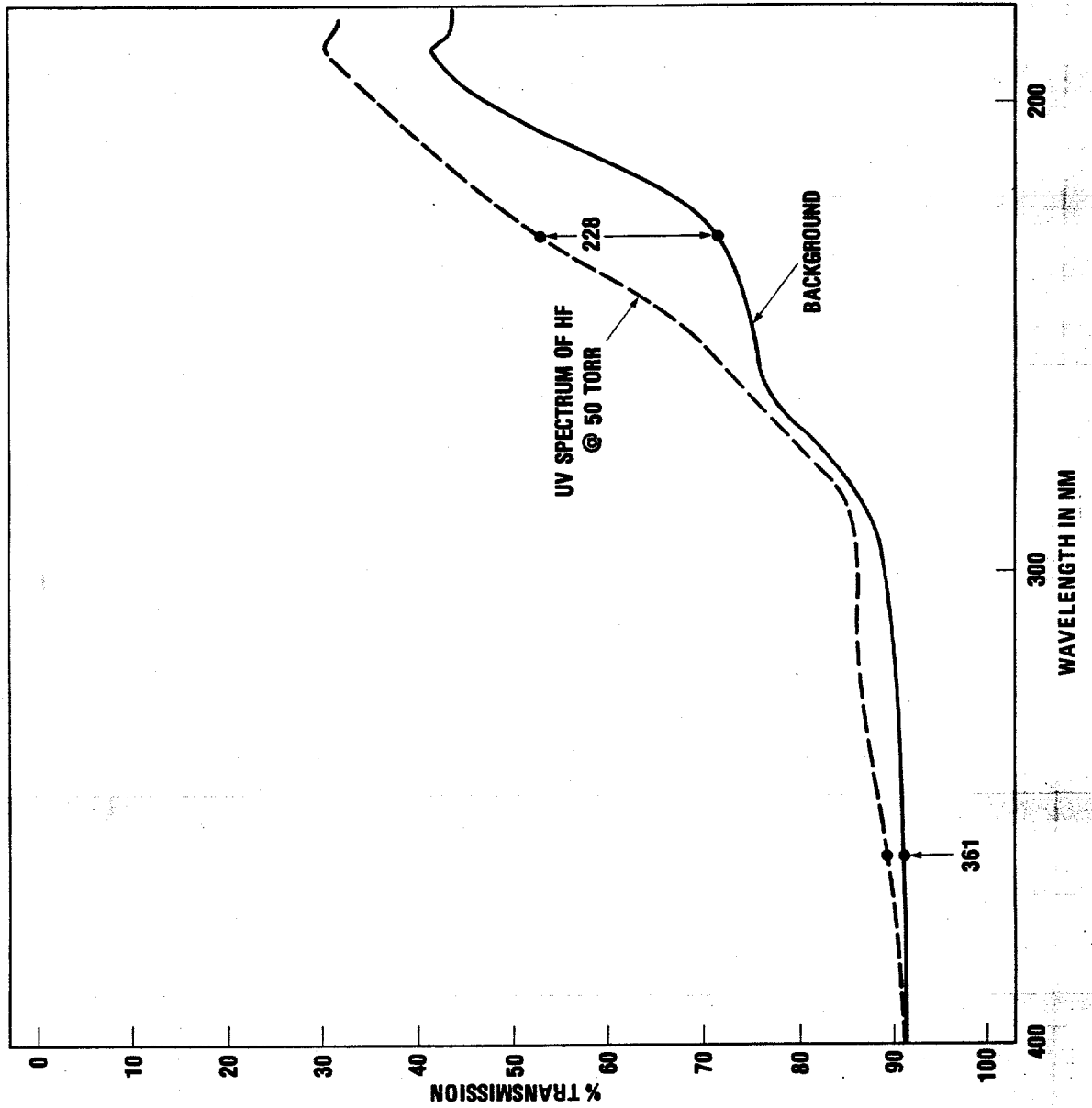
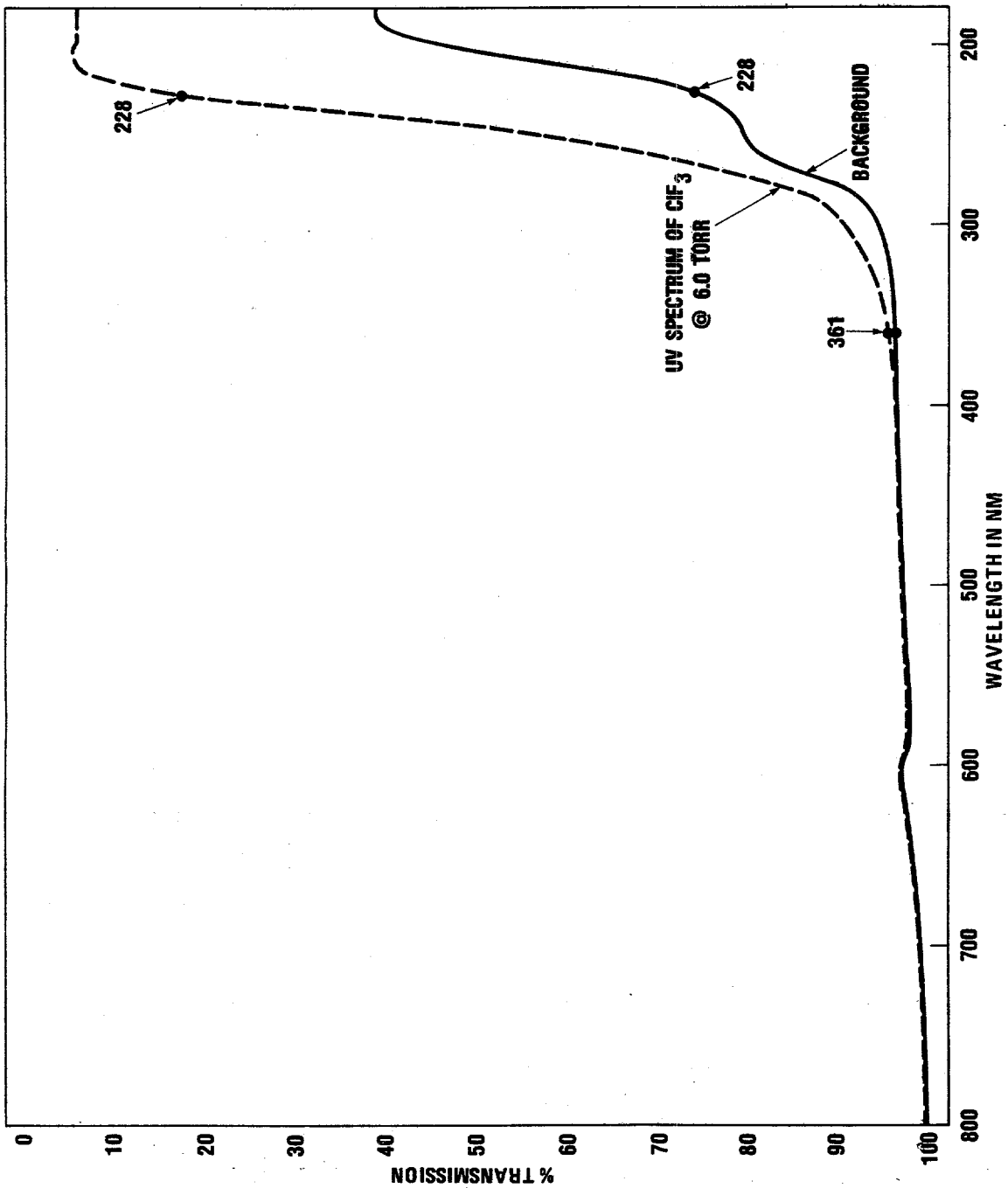


Figure 6
UV SPECTRUM OF F_2 @ 100 TORR

DWG. NO. K/G-82-1133
(U)Figure 7
UV SPECTRUM OF HF @ 50 TORR

DWG. NO. K/G-82-1143
(U)



UV SPECTRUM OF ClF_3 @ 6.0 TORR

Figure 8

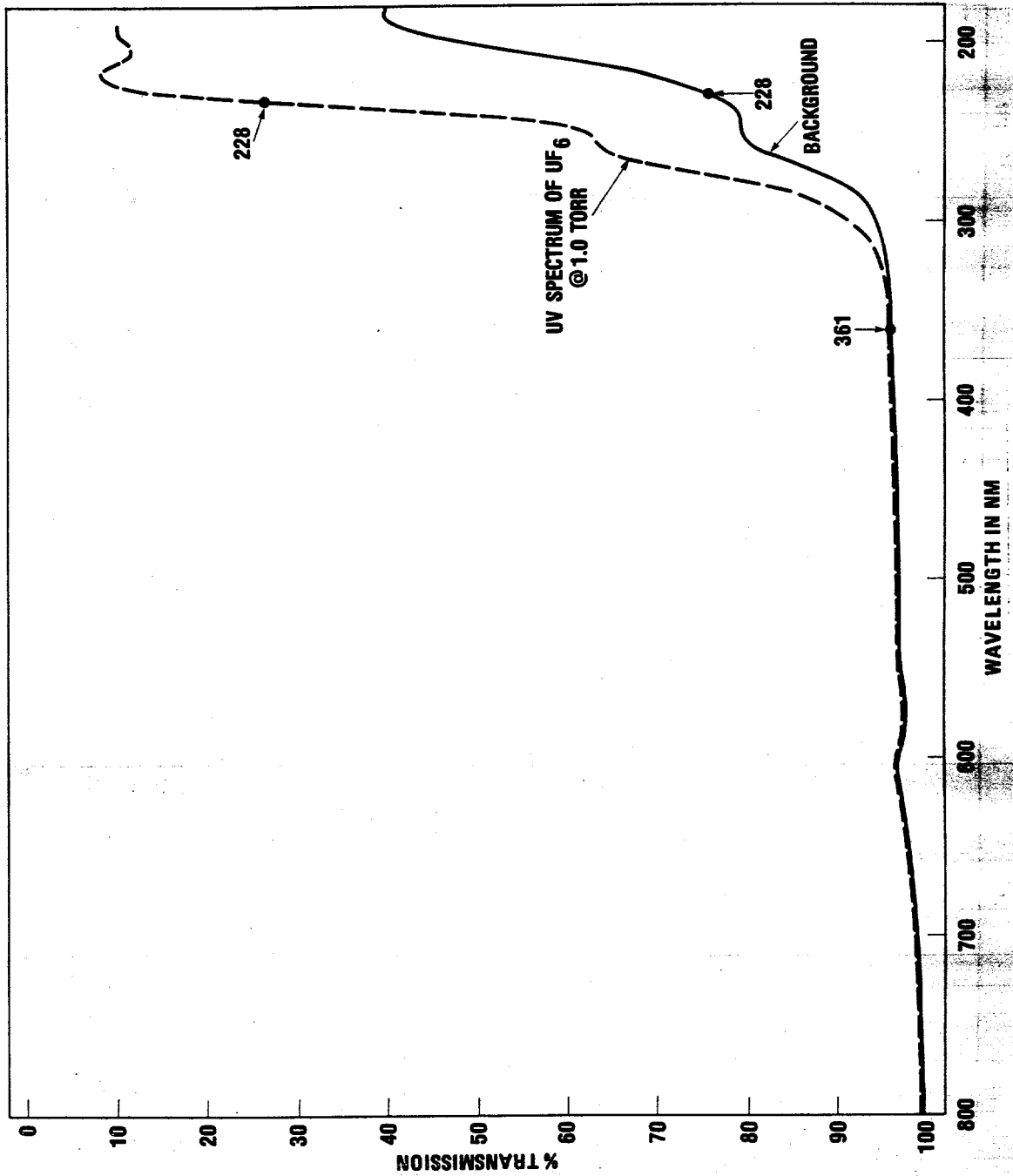
DWG. NO. K/G-82-1144
(U)

Figure 9
UV SPECTRUM OF UF_6 @ 1.0 TORR

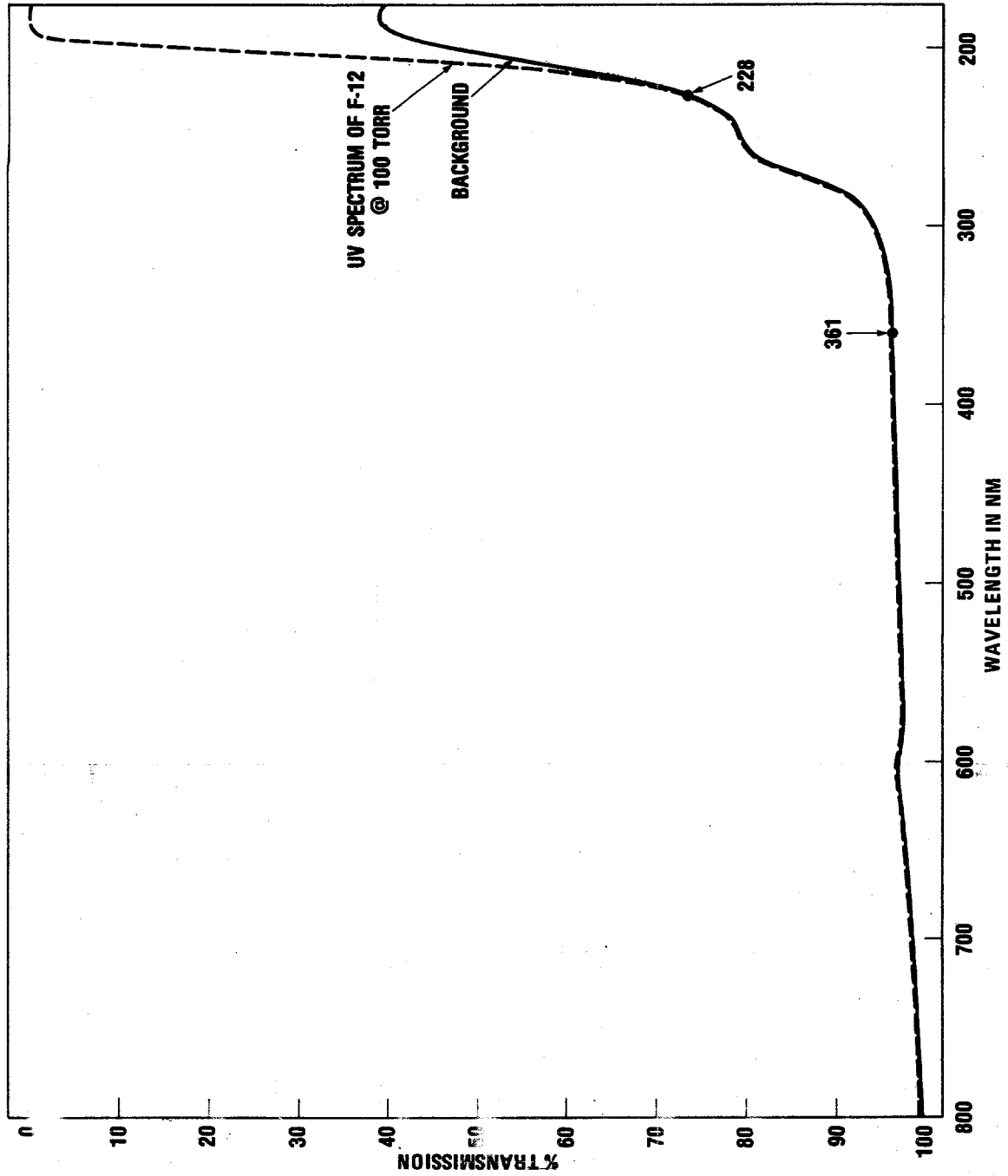
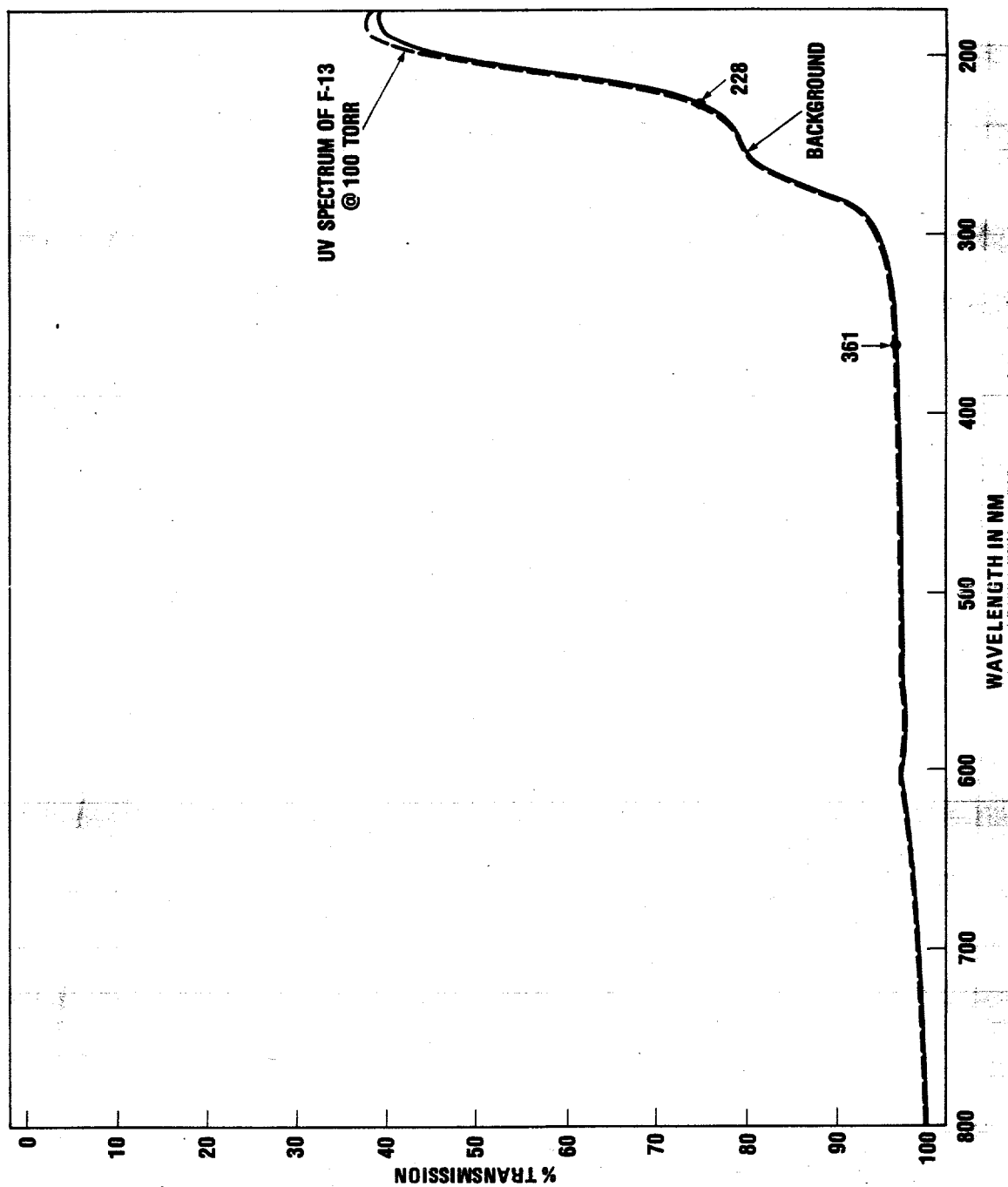
DWG. NO. K/G-82-1142
(U)

Figure 10
UV SPECTRUM OF F-12 @ 100 TORR

DWG. NO. K/G-82-1141
(u)Figure 11
UV SPECTRUM OF F-13 @ 100 TORR

DWG. NO. K/G-82-1140
(U)

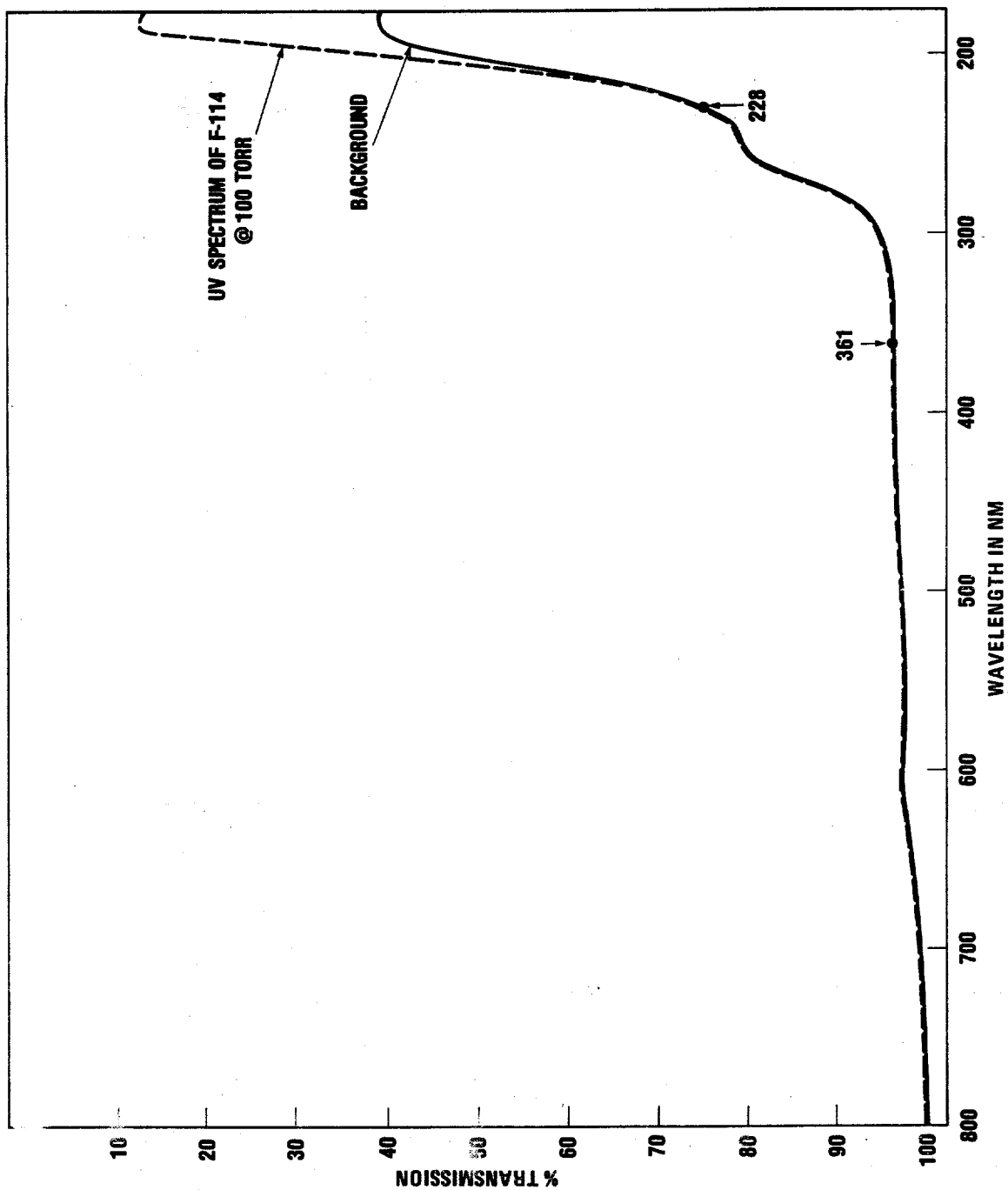


Figure 12
UV SPECTRUM OF F-114 @ 100 TORR

DWG. NO. K/G-82-1139
(U)

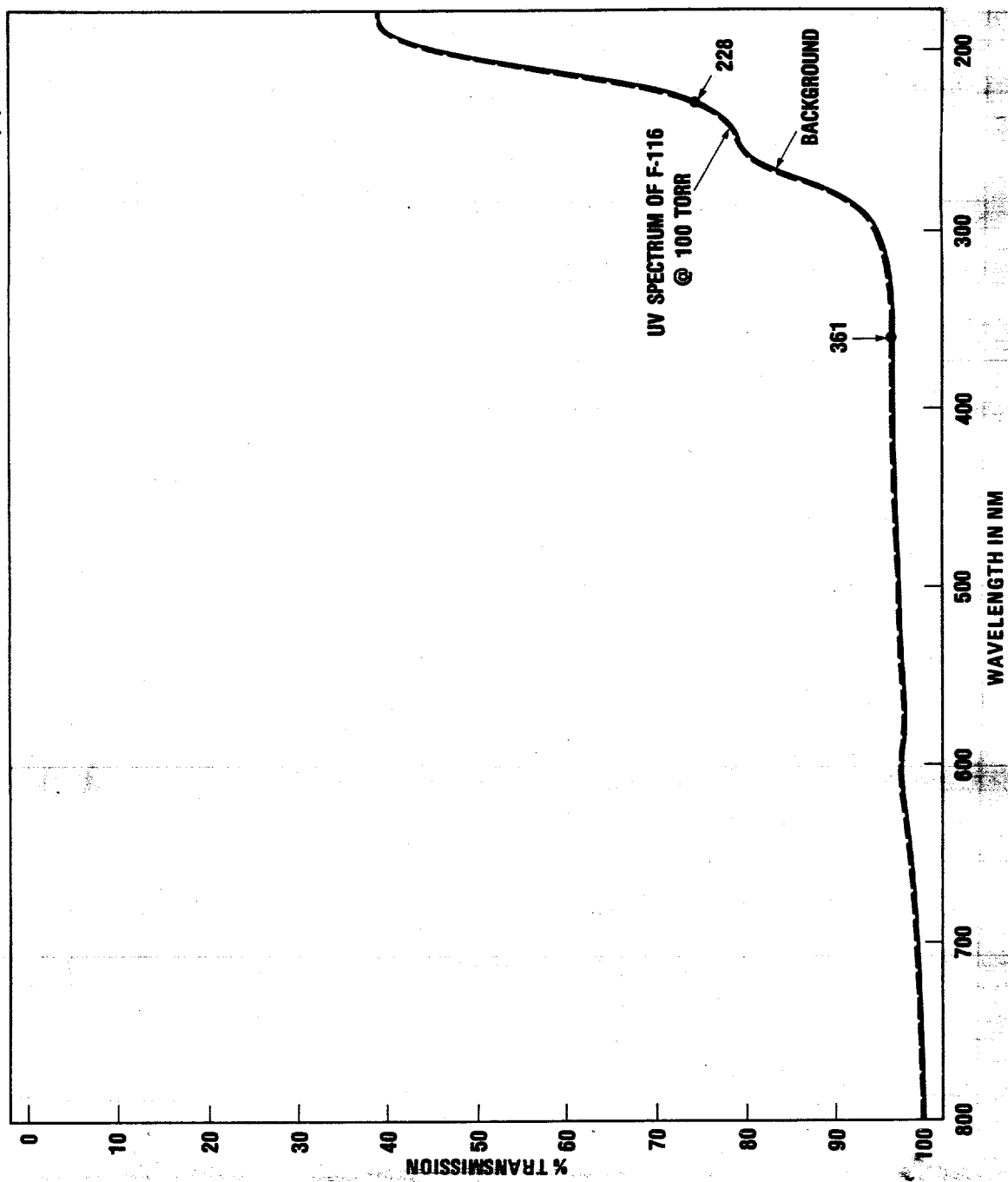


Figure 13
UV SPECTRUM OF F-116 @ 100 TORR

DWG. NO. K/G-82-1138
(U)

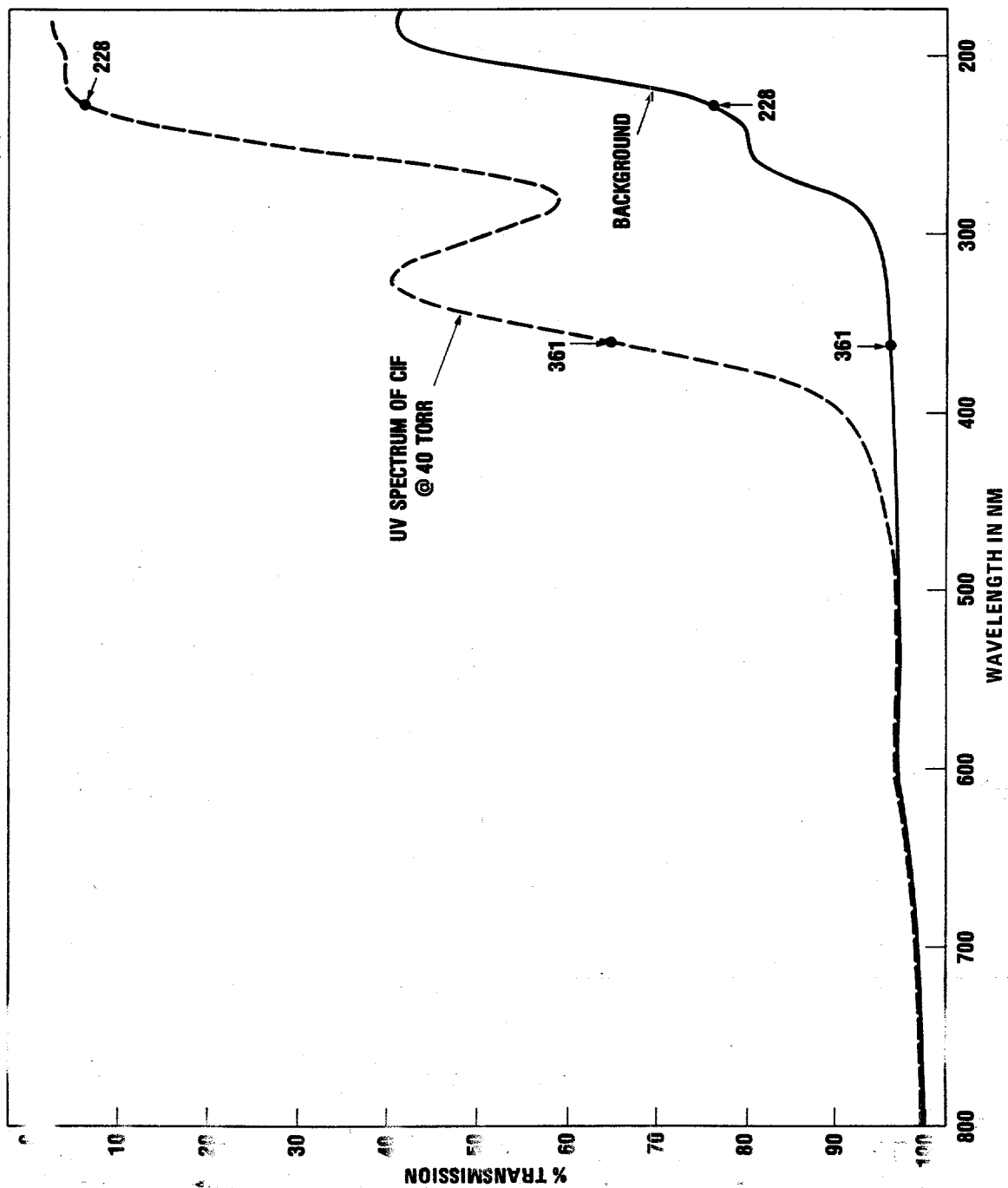
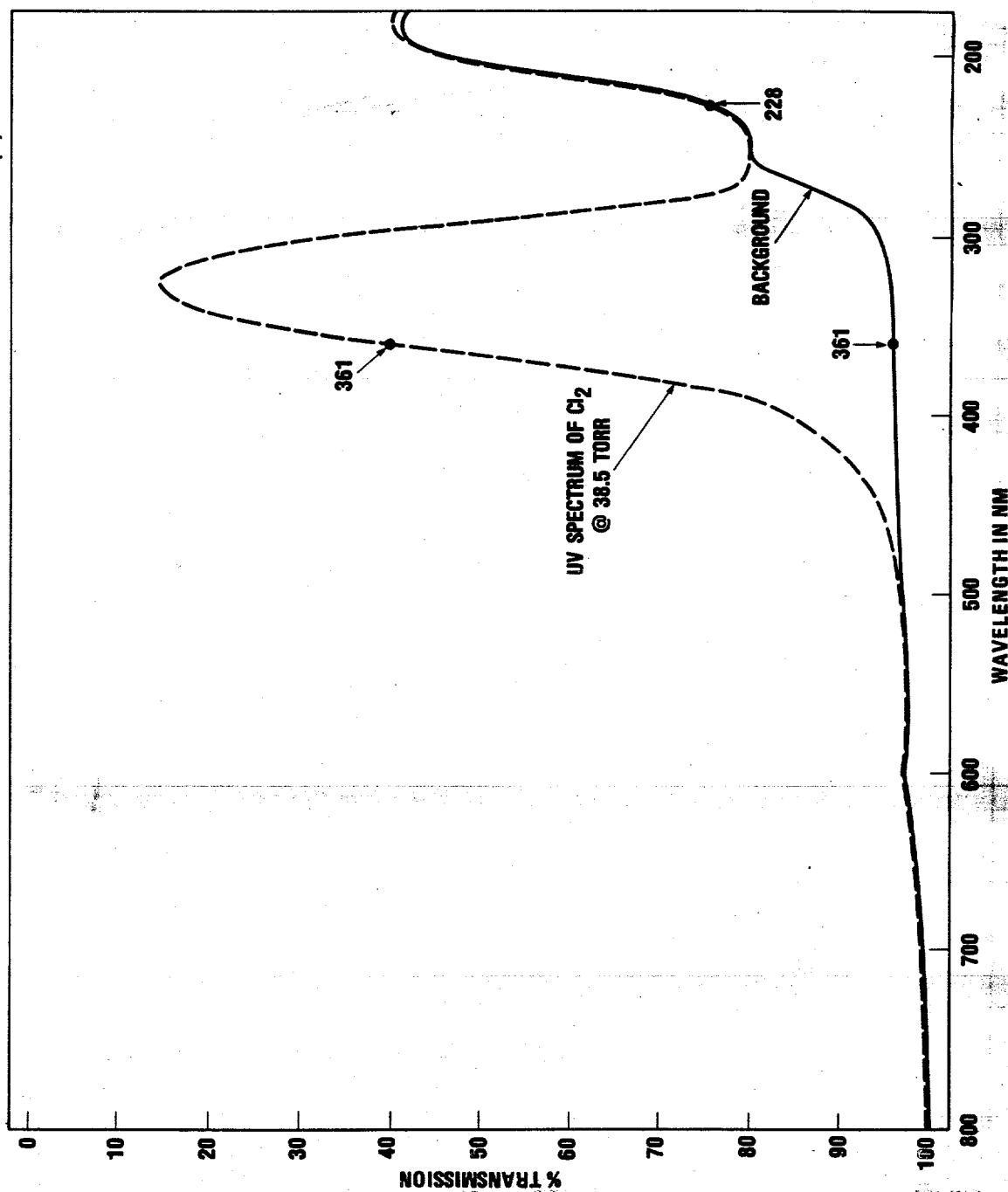


Figure 14
UV SPECTRUM OF CIF @ 40 TORR

DWG. NO. K/G-82-1137
(U)Figure 15
UV SPECTRUM OF Cl_2 @ 38.5 TORR

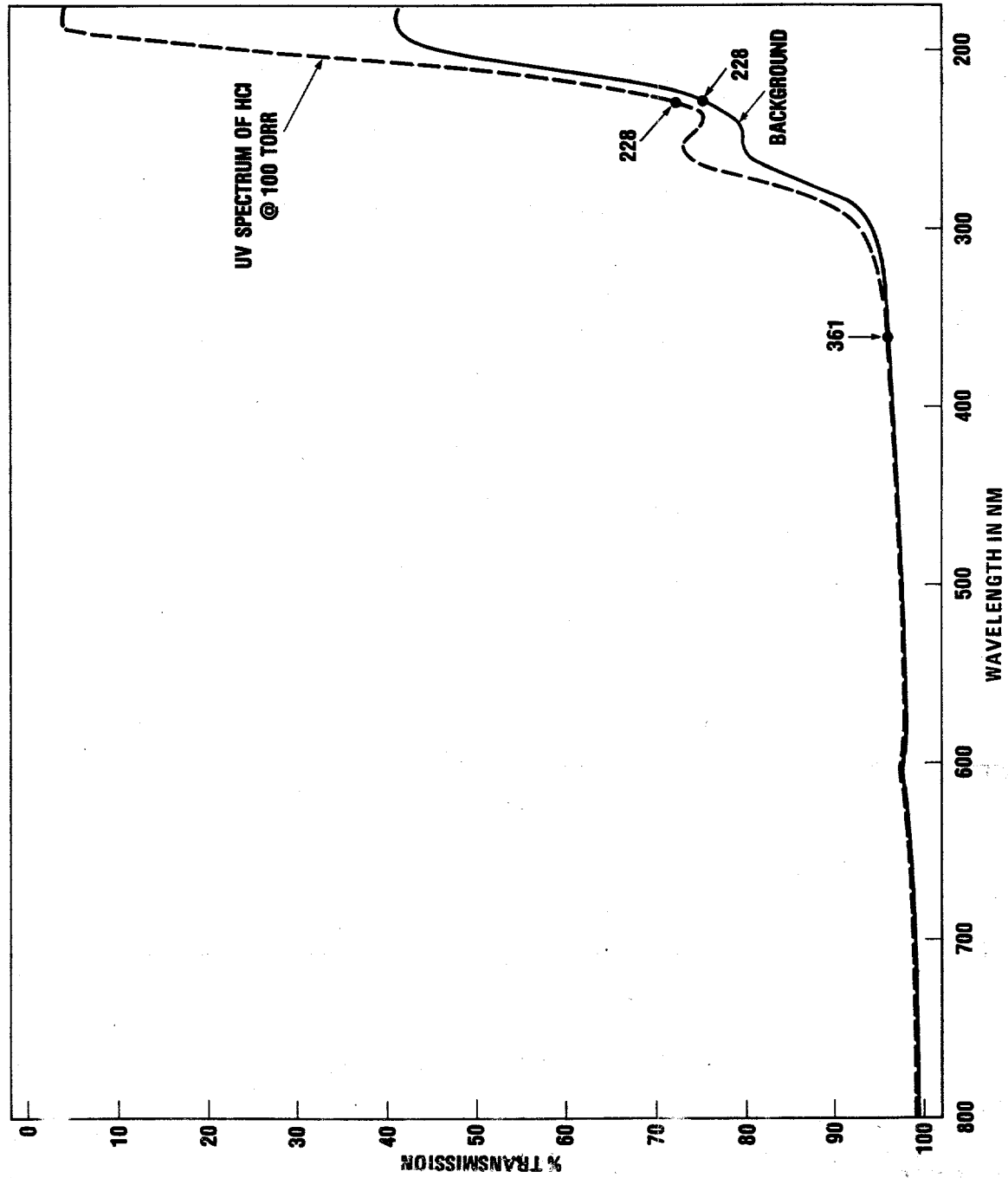
DWG. NO. K/G-82-1136
(U)

Figure 16
UV SPECTRUM OF HCl @ 100 TORR

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